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New Glass Technologies for Enhanced Architectural Surety[®]: Engineered Stress Profiles (ESP) in Soda-Lime-Silica Glass

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Abstract

There is growing awareness of the need to protect building occupants from the effects of malevolent acts, extreme weather, and accidental gas explosions in plants and residential dwellings. A large percentage (85%) of the injuries and fatalities caused by terrorist bombings have been attributed to flying window glass. Numerous fixes have been proposed from the empirical database and field testing by the Department of State, the Defense Threat Reduction Agency, the General Services Administration, the Department of Defense, and other government agencies. Some fixes are being implemented by these agencies. This Sandia National Laboratories project explores enhanced glass performance that can reduce injuries and how the glass affects the overall building response. Sandia National Laboratories has conducted initial blast tests on window glass and there are indications that certain designed flaws and engineered features of the glass, including controlled fracture properties, can be applied that could result in fewer fatalities and injuries to building occupants.

Engineered Stress Profile glass with <u>controlled</u> fracture properties was developed recently by researchers at Penn State (Green et al., 1999) and tested at Sandia National Laboratories. This glass has very high reliability (Weibull modulus = 60), strength of 4 to 5 times that of regular glass, and unusual fracture behavior in that multiple, visible warning cracks are generated before catastrophic failure occurs. The glass also fractures into very small fragments. This property is the primary advantage of the use of stressed glass in an architectural application, as small fragments are less lethal than the large shards produced during failure of regular glass. Another advantage of this glass for applications under sustained loads is that it provides a visible warning that it has reached stresses close to its failure load. The enhanced properties and anomalous behavior were achieved using a double ion exchange process on a specialty glass composition.

The overall objective of this program is to evaluate the feasibility of developing a glass material that can be used effectively in blast environments to reduce injuries to building occupants. Understanding the mechanics and processing of Engineered Stress Profile (ESP) glass is a critical part of this evaluation. Several manufacturing processes are being investigated to determine the viability of producing the type of glass that would be blast-resistant or would fail in a less lethal manner (i.e., greater frangibility, controlled strength, etc). The objective of this year's study was to develop a process for producing Engineered Stress Profile glass using commerciallyy available soda-lime-silica glass. The effort from the first year produced a manufacturing process for commercial soda-lime-silica glass that provides potential performance advantages in applications where Architectural Surety® requirements are critical.

Acknowledgments

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Introduction

Use of glass as an engineering material is limited by its brittle fracture behavior, wide strength variation, and low effective strength under normal use conditions. These characteristics were described by Griffith (1920, 1924) as a result of surface cracks and other flaws in the material that act as stress concentrators. Glass strength is normally controlled by the size of the worst defect, which varies considerably from sample to sample. The larger the crack, the lower the stress is required for it to propagate. The implications of the presence of a large population of flaws are that glass fractures catastrophically, usually at stresses more than one hundred times lower than the theoretical strength, and the variability in the stresses that lead to failure is very high (±25%) (Glass, 1993). The combination of low strength and high strength variability means that engineers who design for applications that could use glass either use very thick glass to achieve high safety factors or decide not to use glass at all.

One technique that has been used to overcome the low strength of glass is to induce a compressive stress in its surface. Two processes have been employed to achieve this stress: either a thermal tempering process, by which the surface is cooled more rapidly than the interior, or an ion exchange process, in which larger ions are substituted for smaller ions in the surface. (This chemical process is often called ion stuffing.) The types of stress profiles that are generated by these two processes are shown in Figure 1.

Stress Profiles in Conventionally Strengthened Glass

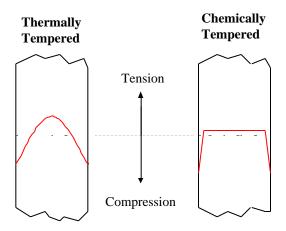


Figure 1. Cross Sections of Glass Plates Showing Residual Stress Profiles Due to Thermal and Chemical Modifications

In the ion-stuffing method of compressive strengthening (Figure 2), small alkali ions in the glass are replaced by larger ions. Thus sodium can replace lithium; potassium or silver can replace sodium, etc. The larger replacement ions take up more volume than the original ions. When the ion-exchanged section is constrained by adjacent non-exchanged glass, it cannot expand to its new natural volume. Instead it develops a compressive stress at the surface, balanced by tensile stress in the non-exchanged region.

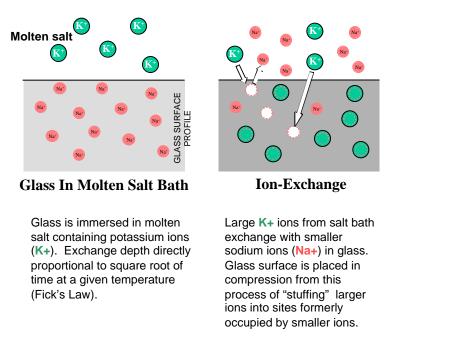


Figure 2. Schematic Diagram of Ion-Exchange Process

Because cracks normally grow under tension, applied tensile stresses must overcome the residual compression in the surface of the glass in order to cause failure. The degree of strengthening can be more than three times the as-received level (Zijlstrra and Burggraaf, 1968). One of the other benefits of compressive strengthening, especially for safety critical applications such as automobile windows and architectural glazing, is that when failure occurs, the glass fragments are much smaller and less shard-like (and hence less lethal) than in regular annealed glass.

Many commercial and defense applications of glasses require high strength; however, the fracture pattern, fragment size, and strength variability, as well as how to control each of these characteristics, have largely been ignored. Although fragments are smaller for glasses with compressive surface stresses than for stress-free glasses, they are still too large for Architectural Surety[®] and other applications of interest. In the past, the only method for controlling glass fragment size has been to try to control the level of interior tension; no efforts have been made to control the fragment shape. In some circumstances, because of the difficulty in controlling the process used to produce the surface compression and the nature of the fracture process itself, the glass does not always completely disintegrate into small fragments, resulting in large joined assemblages of glass fragments (Beauchamp and Matalucci, 1998).

The major problem with using a surface compression strengthening technique is that the strength variability often increases for compression-strengthened glass compared to asreceived glass; the strength variability of ceramics and glasses is already unacceptably large for many applications!

Currently there is wide interest in the behavior of of glass in windows (Blast Effects Mitigation and Injury Outcomes Conference, 2000) and other applications in which control of the fragmentation behavior (smaller and controlled fragment sizes), increased strength, and a significant reduction in the strength variability are desired. Other applications of glass require that it fractures at a very narrowly defined range of stresses and that it fragment into numerous microscopic fragments. These applications include removable valves for the oil industry, architectural glazing to protect building occupants against terrorist bombings, and several defense program uses.

Strategies for increasing the strength and decreasing the strength variability of polycrystalline ceramics are now well known, but there has been little work on doing the same for glasses. One approach for polycrystalline ceramics has been to use microstructural modifications, such as fiber and grain bridging, that produce R-curve behavior (increasing crack resistance) in the material. These modifications produce an apparent increase in the toughness of the material as cracks in it grow. Because glass does not have a microstructure, similar strategies are unavailable. Also, many of the reinforcement strategies used for polycrystalline ceramics are not an option for glasses in which the transparency of the glass is also often an essential feature of its application.

One option in glass has been to design a built-in stress profile that would produce R-curve behavior. Stress profiles have been produced in glass for many years using both ion exchange and thermal tempering processes; however, until recent theoretical analyses were conducted it was not clear what kinds of stress profiles could be used to improve both the strength and the reliability and to produce flaw-insensitive behavior. We now have the theoretical analyses that show what types of profiles will produce the desired behavior. A recent theoretical approach proposed by Tandon and Green (1991 and 1992) suggested that the strength variability of ion exchanged or tempered glass can be very tightly controlled by tailoring the stress profiles to produce the compressive stress maximum below the surface, rather than at the surface. They suggested that certain surface stress profiles would allow a crack to be arrested and that there would be a reduction in the strength variability.

One demonstrated way to achieve the desired stress profile is to use a two-step ion exchange process (Sglavo et al., preliminary patent disclosure to produce an Engineered Stress Profile (ESP) in which there is a high compressive stress just below the glass surface, rather than at the surface. (see Figure 3). According to work by Green (1984), the extent of the compressive layer below the glass surface has a significant effect on the strength and reliability, often more important than the level of maximum compressive stress.

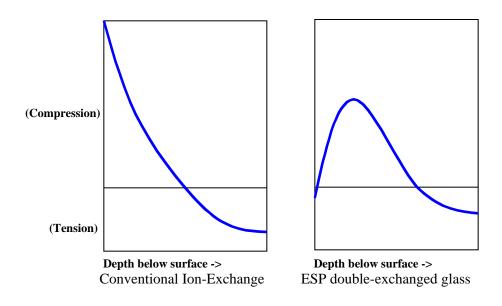


Figure 3. Stress Profiles of Ion-Exchanged Glass

In experiments by Green et al. (1999 and 1999) and Sglavo and Green (in prep.), this type of 'buried' compressive stress profile has shown a number of beneficial effects in terms of strength, reliability, flaw-tolerance, and fracture behavior. The double ion exchange process was demonstrated on a specialty glass (sodium aluminosilicate). In the first step, potassium ions from a molten salt bath were exchanged for sodium ions in the glass. In the second step, some of the introduced potassium was removed from the surface by an exchange with sodium ions. Strengths were measured for glasses made in this manner and very low strength variability was observed Green et al., 1999; Green et al., 1999; Glass et al., 2000). The glass has strength four to five times that of regular glass and Weibull modulus values as high as 60. The benefits of a Weibull modulus at this level are shown in Figure 4. A designer's confidence in the glass's ability to survive or fail at a given stress is increased significantly with higher Weibull modulus. For an application in which the glass must sustain 80% of the average failure stress, ESP glass with a Weibull modulus of 60 has only a one or two in one million chance of failing. In contrast, regular annealed glass (Weibull modulus = 5) has a 30% failure probability.

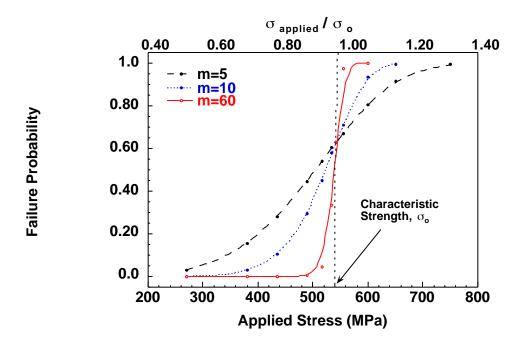


Figure 4. Failure Probability vs. Applied Stress for Various Weibull Moduli (m) (ESP glass, with m = 60, has a dramatic increase in failure probability only at the average failure stress, in contrast to regular glass, with m = 5 to 10, which has a high failure probability at stresses above and below the characteristic failure stress.)

The ESP glass also fractures into very small fragments. This is one of the primary advantages of the use of pre-stressed glass in an architectural application, as small fragments are less lethal than the large shards produced during failure of regular glass. Also, during strength testing, cracks could be seen growing in the surface of the glass and then arresting. An increased load was required to initiate the next crack. It propagated slowly and then arrested. This process continued until there was a visible array of cracks indicating that failure was imminent. The material shows some 'fail-safe' behavior, even though it is a brittle material. Such behavior is extremely unusual and could be exploited in many technological applications of glass.

Added benefits of the high strength and reliability are that there would be less breakage during installation and that thinner glass could be used, resulting in reduced cost and weight. If overall Architectural Surety® considerations dictate that the windows not be strengthened to this degree, the strength can be reliably controlled to achieve a consistent value that is lower, but still stronger than regular glazing if that proves to be beneficial. Another advantage of a high-strength glass with low strength variability is that an actuator could be incorporated into the design of the frame that would cause the glass to fail at a very specific pressure under explosive loading. This would relieve some of the load on the overall structure and cause glass failure before it gains a significant amount of the strain energy that carries fragments into the building.

The goal of the present study was to develop Engineered Stress Profiles (ESPs) in sodalime-silica (SLS) glass to achieve high strength, low strength variability, and controlled fragmentation. Previous ESP glass research focused on soda-aluminosilicate glasses, which have a higher diffusion rate for alkali ions and therefore offer more rapid, deeper exchange. However, aluminosilicate glasses are produced in relatively small quantities at considerable expense and are used only for specialty applications. Although the double ion exchange method has been successfully used for a specialty glass composition, modified techniques may be required for SLS glasses because of the low diffusion coefficients of the ions in this glass during the ion exchange process. Techniques such as ion implantation or field-assisted exchange could be used to introduce ions that are not readily exchanged using a molten salt bath, or to produce modified surfaces with very controlled depths.

The effects of the ESPs on the strength, strength variability, and fragmentation behavior will be studied for SLS glass for different types of loading conditions, both in terms of the type of loading (e.g., flexural vs. tensile) and the loading duration (sustained, static, dynamic, and explosive loading). The effect of loading rate is very important at both ends of the scale and is not understood under very rapid loading rates, especially for glasses with compressive surface stresses. As the surfaces of glasses usually contain numerous flaws with different sizes and character, their effects on the behavior of the glass and their interactions with each other and the residual stress field during stable crack propagation also need to be evaluated.

The ultimate goal of this program is to understand the behavior and benefits of using ESP glass in Architectural Surety® applications to improve our ability to protect personnel against terrorist activities, such as bombings of federal buildings and extreme weather conditions. We also expect to demonstrate that a new class of glasses can be produced with highly controlled fracture properties that will provide unique capabilities for Defense Programs and commercial applications. The increased reliability of the glass also increases the confidence of designers in the use of glass for both conventional and innovative applications. By developing an ESP process for widely available SLS window glass, ESP glass products can be applied to larger markets at reduced cost, thus changing a limited-use, specialty product into one that can benefit many industries and individuals. Our efforts include developing collaborations with glass manufacturers and the architects, design engineers, and agencies interested in the use of glass, especially in applications in which personnel safety can be enhanced through using a glass with improved properties.

Impact of Work

Validated information about glass behavior and options for enhancing glass performance are important for glass manufacturers; users in the transportation, food and oil industries; Architectural Surety® applications; and defense program applications. For example, automotive glass producers are very interested in how to fabricate glasses that fracture into small fragments with a narrow fragment size distribution. The food packaging industry is interested in reducing the weight of glass containers without jeopardizing consumer safety. Halliburton Energy Services has supported work at Sandia National Laboratories on removable valves. There is considerable interest in Architectural Surety® for ensuring that windows do not fail, or fail in a graceful manner, under extreme weather conditions or terrorist attack. There are similar interests in either ensuring or preventing failure of brittle materials for defense program applications, such as stronglinks and weaklinks.

To be able to design with a glass material that can be counted on to fail or survive in specified conditions will provide unique opportunities in weapons systems and numerous commercial applications. This work will also extend our capabilities for understanding brittle fracture under complex loading conditions.

Experimental

Materials and Equipment

The glass used in the experiments is Starphire, an architectural window glass manufactured by PPG Industries, Inc. with the composition 73% SiO₂, 15% Na₂O, 10% CaO, and 2% trace elements by weight.

Mini-30 and Mini-60 Salt Bath Furnaces from Kirk Optical Co. were used for ion-exchange, as well as conventional laboratory furnaces with welded nickel salt bath vessels. Within the vessels, samples were held in stainless steel wire-mesh racks. Temperature was measured by electrically isolated K-type thermocouples attached to the sample racks.

Sample Preparation

The samples (see Figure 5) used in these experiments were cut from annealed 3.2-mm-thick Starphire SLS glass sheet using a diamond saw, prior to ion-exchange treatment. Biaxial flexure specimens were cut as 25-mm squares. Four-point bend specimens were cut to dimensions of 75 mm by 6.5 mm. The tensile edges of the 4-point bend specimens were then ground to a rounded profile by wet grinding on an abrasive belt.

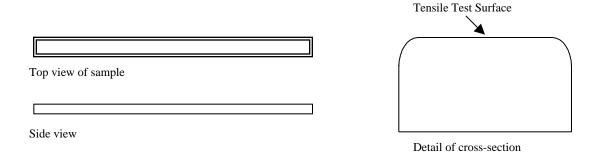


Figure 5. Detail of 4-Point Bend Specimen

Previous work has shown that sample preparation is very important in achieving good results with ESP glass. In particular, corners of the tensile surface must be rounded in order to prevent premature failure from corner cracks during bend testing.

Ion-Exchange Processing

The samples were placed in a stainless-steel wire-mesh carrier, dried in air, and put in a bath of molten potassium nitrate (KNO₃, 99.9% purity) at 450 °C for 48 hours. Temperature was measured using a thermocouple inserted into the wire carrier. Previous work (Abrams and Green, unpublished) showed that these conditions had the potential for producing desirable stress profiles. The samples were held in heated air within the furnace for 15 minutes before and after treatment in order to prevent fracture from thermal shock.

After cooling, the samples were washed in water to remove any residual salt, dried, then placed in the second ion-exchange bath, with a composition of 2 parts KNO₃ to 1 part NaNO₃ by mass, at a temperature of 400 °C for 30 minutes. It is this second ion-exchange process that reduces the potassium concentration at the glass surface, producing the characteristic hump in the ESP glass stress profile.

Optical Stress Measurement

In order to accurately measure the stress distribution in the processed samples, an optical retardation technique was used. Because stressed glass is birefringent, showing a change in refractive index proportional to stress, the stress can be determined by measuring the birefringence for a sample of given length, using techniques by Beauchamp and Altherr (1971).

The experimental setup (see Figure 6) utilizes a sample placed between crossed polarizing filters. The birefringence caused by the stresses within the sample retards and changes the polarization of light passing through it, allowing light to be seen at the far end. The degree of retardation can be accurately measured using a Babinet compensator and a set of optical retarder plates.

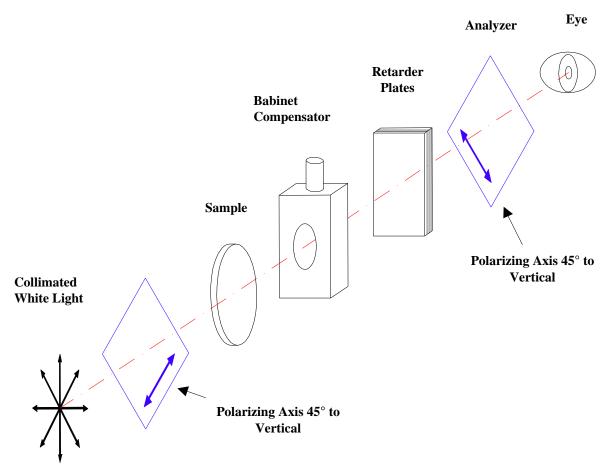


Figure 6. Schematic of Optical System Used to Measure Retardation in Stressed Glass Samples

Because the compressive layer near the surface of the glass is relatively narrow, on the order of ~50 microns, it is difficult to optically observe the birefringence it produces directly. Instead, the birefringence due to the balancing tension at the center of the glass is measured, and the change in central tension is observed as outer layers are etched away in HF acid, as shown in Figure 7.

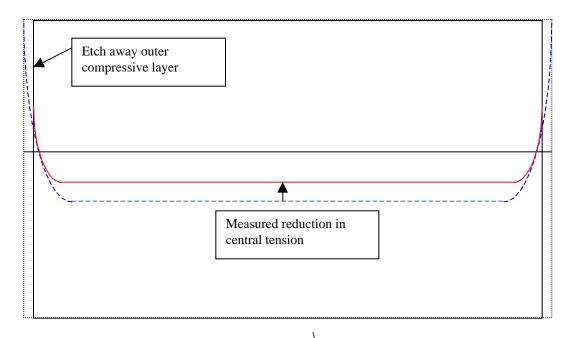


Figure 7. Change in Central Tension Measured as Surfaces Are Removed by Acid Etching

Strength Testing

Mechanical strength testing, including conventional 4-point bend testing and ring-on-ring biaxial flexure testing, was used to measure the strength of ESP glass specimens. Several 4-point bend specimens were not tested to failure, but were instead loaded to specific stress levels, then unloaded and etched with HF acid to reveal any crack patterns that developed prior to final fracture.

Results

The following graph (Figure 8) compares strengthsh for soda-lime-silica glass in the annealed state, after a conventional ion-exchange, and after a double ion exchange (ESP glass), using the ion exchange conditions specified earlier.

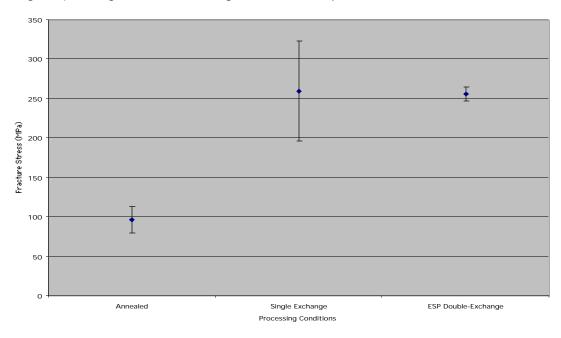
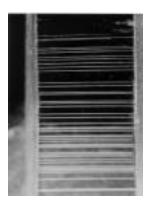
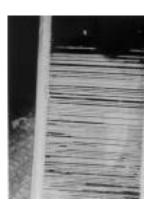


Figure 8. Strengths for Processed SLS Glass

Note that the ESP glass shows high strength as well as very good reliability, with a standard of deviation at ~3% of mean value, a very low value relative to the annealed and single exchange conditions.

The presence of multiple small cracks, which develop in the glass as it approaches fracture stress indicate that the strength of the glass is insensitive to the size of the largest flaws. Below are photographs (Figure 9) of ESP glass, stressed in 4-point bending, then etched to help reveal patterns of multiple, parallel cracks. This cracking effect begins at less than 50% of the mean fracture stress and continues as the applied stress increases, reaching an average spacing of 92 microns at 90% of the fracture stress. Note that without etching the cracks become visible to the naked eye at 85-95% of fracture stress, providing a useful warning of imminent failure.





(a) (b)
Figure 9. Tensile Surface of SLG Glass at a) 60% of Fracture Stress and b) 85% of Fracture Stress

Figure 10 shows the stress profile for an ESP glass sample, obtained using optical retardation measurements. Note the increasing compressive stress below the surface, with a maximum at approximately 11 microns in depth.

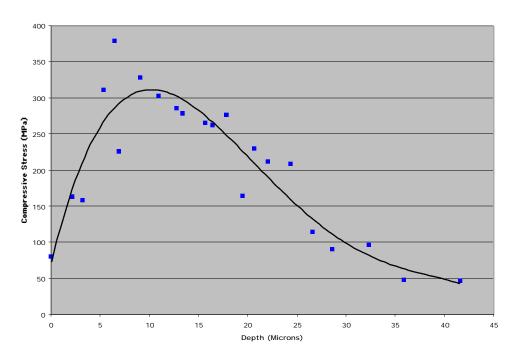


Figure 10. Stress Profile Measurements Using Optical Retardation (Central tension ~5 MPa)

Figure 11 shows a partial stress profile for ESP glass with an extended 2^{nd} exchange treatment, 45 minutes instead of 30. The position of the compressive peak has shifted deeper (~18 µm) beneath the glass surface, as expected. Control of the duration, temperature, and bath composition of each exchange step provides a great degree of control over the peak size, shape, and depth below the surface, allowing a wide range of useful properties.

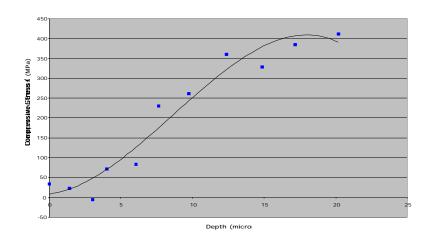


Figure 11. Partial Stress Profile for Sample with Extended 2nd Ion-Exchange (Central tension ~5 MPa)

Previous fracture strength measurements of soda-aluminosilicate ESP glass made at various loading rates showed an unusual increase in strength for slower loading. Preliminary results with SLS ESP glass appear to indicate the same strength increase. This effect is opposite to the loading-rate effects observed in conventional, annealed, tempered, or chemically strengthened glass (Hagy, 1966) and represents another opportunity for future study.

Preliminary work on the abrasion resistance of ESP glass using ball mill abrasion tests as per ASTM C 158 indicated that ESP glass does not significantly lose strength after abrasion by silicon carbide particles. Although scratches are observed on the glass surface, 4-point-bend strength appears unaffected. The interaction of abrasion damage with the multiple cracks normally developed in the glass under high stress is unknown and requires further study.

Conclusions

SLS ESP glass shows high strength with exceptional reliability in 4-point bend testing, with standard deviation at 2-3% of the mean fracture stress. This quality makes it useful for structural and new applications, significantly reducing the chance of failure at low stresses and ensuring failure above a critical stress level. This high reliability can be useful for "command-break" applications such as valves, where it is necessary that the material fracture at a particular stress level.

The multiple cracking patterns shown by ESP glass before fracture provide a progressive warning prior to failure, something very uncommon in glass and ceramic components. Further study is needed to determine what parameters control the number and depth of the cracks and how they affect the unusual mechanical properties of the material.

Results show that by changing ion-exchange processing parameters, the stress profile present in the final glass can be carefully controlled. Theoretically, by driving the profile more deeply below the surface, excellent abrasion resistance can be obtained. By raising the maximum stress, higher strength is achieved. Further work is required to more closely understand the relationship between ion-exchange time, bath composition and temperature; and the final properties of the strengthened glass.

The two-step ion exchange process provides broad flexibility in terms of engineering the stress profile to optimize strength, reliability, and fragmentation behavior for different glass compositions. We will continue to improve our ability to engineer stress profiles and glass behavior to satisfy new application requirements and to determine what properties best satisfy requirements for controlled failure under blast loading conditions for Architectural Surety[®] applications.

Future Work

Future work includes:

- Further stress profiling in ESP glass, to link processing conditions to final stress state
- Fractography of ESP glasses, leading to a better understanding of fracture behavior in these glasses
- Measuring subcritical crack growth and comparing with behavior of aluminosilicate glass
- Testing ESP glass under rapid/explosive loading

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An upcoming publication related to this Laboratory Research and Development project is E. K. Beauchamp's "Fracture Behavior of Double-Ion-Exchanged Glass," to be published in the Proc. of the Fractography of Glasses and Ceramics Conf. IV, Alfred, NY, July 9-12, 2000.

Appendix

ESP (Engineered Stress Profile) Glass – Unique Opportunities for Performance and Reliability

by

S. Jill Glass, Ed K. Beauchamp, Clay Newton, and Ron Stone

ESP (Engineered Stress Profile) Glass -Unique Opportunities for Performance and Reliability

M otivation—There are many aspects of glass that we take for granted such as its transparency, its formability, and the abundance and cheapness of the raw materials. One property not taken for granted is its low strength and reliability. Glass is the classic brittle material with extreme sensitivity to the presence of surface flaws and catastrophic failure. Once the stress exceeds that required to activate the most severe flaw, which is not easily detectable, failure occurs instantaneously without warning. The wide flaw size distribution in glass leads to a wide fracture strength distribution. Flaws are either intrinsic to the processing of the glass or are surface damage introduced after processing. As a result glass is rarely considered for structural applications and large safety factors are built into any design where strength and reliability are critical. The introduction of residual surface stresses is commonly used to strength increase the and modify the fragmentation behavior of safety glass. The small cube-like fragments of pre-stressed glass are far less lethal than the large dagger-like shards that are typical of the fracture of annealed glass. Unfortunately the surface modification of pre-stressed glass does not increase reliability; it often increases strength scatter even further.

A ccomplishment--A new approach for strengthening and dramatically increasing glass reliability has been developed and implemented for both specialty compositions and for regular soda lime silicate (SLS) glass. Regular ionexchanged glass and thermally tempered glass have the compressive stress maximum right at the surface. The new process uses a two-step ion exchange. During the 2nd step some of the large ions introduced in the 1st exchange step are removed, partially relieving the surface stress and producing a compressive stress maximum below the surface. At significant levels of the applied stress (relative to the fracture strength) a single surface crack starts to grow into the glass. The crack encounters increasing resistance to

propagation as it penetrates into the increasing compressive stress field. Finally the magnitude of the compressive stress arrests the crack and it turns away from its initial trajectory. As the applied stress increases further another surface crack begins to propagate and is then arrested in the same manner. Fig. 1 shows ESP glass that contains an array of arrested cracks. This process is repeated until a critical value of the applied stress is reached. The failure strength is not dependent on the size of the worst flaw, but on the details of the stress profile. Thus the strength distribution is not dependent on the flaw size distribution and is very narrow compared to that of regular glasses and ceramics. A typical glass has a low Weibull modulus, e.g., m=5-10. ESP glass has values as high as 60. The two-step ion exchange process provides broad flexibility in terms engineering the stress profile to optimize, strength, reliability, and fragmentation behavior for different glass compositions. We will continue to improve our ability to engineer stress profiles and glass behavior to satisfy new application requirements.

 ${f S}$ **ignificance**—For the first time we have a glass that is both strong and dependable, cracks non-catastrophically, and fractures into small fragments. A designer's confidence in the glass's ability to survive or fail at a given stress is increased significantly as shown in Fig. 2. In an application where the glass must sustain 80% of the average failure stress, ESP glass with m=60 has an only one two in one million chance of failing. In contrast regular annealed glass has a 30% failure probability. ESP glass also shows remarkable resistance to contact damage, the primary factor in strength degradation for glazing applications where wind-borne debris causes damage. Engineered stress profiles can be produced with processes that allow great flexibility with respect to glass composition and performance optimization, providing unique opportunities for new glass applications.

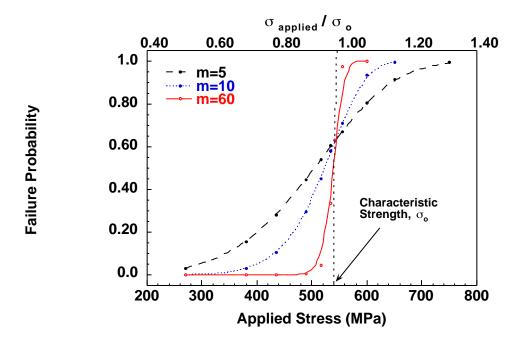


Fig. 1. Failure probability vs. applied stress for various Weibull moduli, m. ESP glass, with m=60, has a dramatic increase in failure probability only at the average failure stress, in contrast to regular glass (m=5-10), which has a high failure probability at stresses below the failure stress.

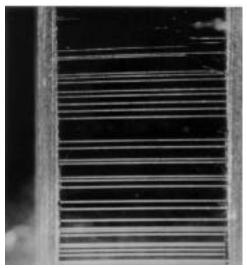


Fig. 2. Soda lime silicate glass with non-catastrophic cracks formed prior to failure.

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